



# N<sub>2</sub>O decomposition over K-promoted Co–Al catalysts prepared from hydrotalcite-like precursors

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## ABSTRACT

N<sub>2</sub>O decomposition was investigated over a series of K-promoted Co–Al catalysts. The activity tests showed that doping with K greatly enhanced the catalytic activity of the Co–Al catalyst, and the enhancement was critically dependent on the amount of K and the calcination temperature. When the catalyst had a K/Co atomic ratio of 0.04 and was calcined at 700–800 °C, a full N<sub>2</sub>O conversion could be reached at a reaction temperature of 300 °C. Moreover, even under the simultaneous presence of 4% O<sub>2</sub> and 2.6% water vapor, such high-temperature treated K/Co–Al catalyst exhibited high reactivity and stability, with the N<sub>2</sub>O conversion remaining at a constant value of 92% over 40 h run at 360 °C. In contrast, non-doped Co–Al catalyst showed a severe activity loss under such reaction conditions. A combination of characterization techniques was employed to reveal the promoting role of K and the effect of calcination temperature. The results suggest that doping with K increases the electron density of Co and weakens the Co–O bond, thus promoting the activation of N<sub>2</sub>O on the Co sites and facilitating the desorption of oxygen from the catalyst surface. High-temperature calcinations made the desorption of O<sub>2</sub> proceed more readily.

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## 1. Introduction

Nitrous oxide (N<sub>2</sub>O) abatement is attracting attention due to its greenhouse effect and ozone-depleting action [1]. N<sub>2</sub>O is produced from various sources, both natural and related to human activities. Anthropogenic sources are associated with the production of adipic acid and nitric acid [2] and combustion of municipal and industrial waste in fluidized bed reactors [3]. Heterogeneous catalytic decomposition of N<sub>2</sub>O is a suitable solution in many of the anthropogenic emission sources, and various catalytic formulations have been proposed thus far, including supported and unsupported metals [3–6], pure and mixed oxides [7–11], and zeolitic systems [12–14]. Among them, cobalt oxides have been found to be very efficient for the decomposition of N<sub>2</sub>O [9,10].

Recent studies have found that the residual alkali metals in the Co-based catalysts, which were introduced during the precipitation, caused a significant increase of catalytic activity. For example, Ohnishi et al. [15] have found that the sodium content remaining in the Co<sub>3</sub>O<sub>4</sub> catalyst was the determining factor controlling the activity

and the optimal Na/Co molar ratio was  $3.8 \times 10^{-3}$ . Similarly, Xue et al. [16] observed that the presence of residual K in Co<sub>3</sub>O<sub>4</sub>–CeO<sub>2</sub> which was prepared by co-precipitation with K<sub>2</sub>CO<sub>3</sub> as the precipitant improved largely the catalytic performance. Motivated by these experimental findings, Asano and co-workers [17] prepared K-doped Co<sub>3</sub>O<sub>4</sub> catalyst by impregnation of KNO<sub>3</sub> on CoCO<sub>3</sub>, in which the alkali content could be finely tuned. They concluded that the number of active sites increased and desorption of oxygen was promoted by the addition of K to the Co<sub>3</sub>O<sub>4</sub>, which resulted in an enhanced activity for N<sub>2</sub>O decomposition. In addition to the promotional effect of Na and K on Co<sub>3</sub>O<sub>4</sub> catalyst, Pasha et al. [18] also observed that the addition of an appropriate amount of Cs to NiO could weaken the Ni–O bond, and the Cs-modified NiO catalyst exhibited higher activity for N<sub>2</sub>O decomposition compared to bulk NiO.

Calcined hydrotalcites containing cobalt, such as Co–Al [9,10,19], Co–Mg–Al [20] and Co–Rh–Al [9,20], etc., showed good catalytic activities in the N<sub>2</sub>O decomposition. One additional advantage of this type of catalysts over pure Co<sub>3</sub>O<sub>4</sub> is their high thermal stabilities and large surface areas [9], which makes them as promising candidates for industrially valuable catalysts for N<sub>2</sub>O decomposition. However, most of the hydrotalcite-derived mixed oxide catalysts reported so far are not efficient enough for the commercial exploitation, in particular under the presence of both

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O<sub>2</sub> and steam. In view of the remarkable enhancement of catalytic activity of Co<sub>3</sub>O<sub>4</sub> by the doping of alkali metals, in the present work, we systematically investigated the effect of doping alkali metals on the catalytic performance of hydrotalcite-derived Co-Al mixed oxide. It was for the first time found that high-temperature (700–800 °C) calcination of the K-promoted Co-Al hydrotalcites could produce a highly active and thermally stable catalyst with good tolerance to O<sub>2</sub> and steam.

## 2. Experimental

### 2.1. Catalyst preparation

Hydrotalcite precursors were prepared by co-precipitation method as reported [21]. An aqueous solution containing appropriate amounts of metal nitrates (Co<sup>2+</sup> + Al<sup>3+</sup> = 0.9 mol/L, Co/Al = 3) was added dropwise to an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (CO<sub>3</sub><sup>2-</sup>/Al<sup>3+</sup> = 2.9) with vigorous stirring at 35 °C. The pH of the mixture was kept at 10 by adding 3 M NaOH aqueous solution. The resulting suspension was aged at 65 °C for additional 18 h. The product was filtered, washed with a large amount of de-ionized water to remove residual sodium and nitrate and finally dried at 85 °C for 20 h. Alkali metals were doped on the hydrotalcite precursors by incipient wetness impregnation with an aqueous solution of the corresponding metal nitrates. The final alkali metal-doped and non-doped Co-Al mixed oxides were obtained by calcining the corresponding hydrotalcite precursors at 500 °C for 6 h, and denoted as M/Co-Al-500 (M refers to the alkali metal) or Co-Al-500, respectively. In order to investigate the effect of calcination temperature, we also calcined the hydrotalcite precursors at different temperatures. The catalysts are denoted as M/Co-Al-Y (Y refers to the calcination temperature).

For comparison, K/Co<sub>3</sub>O<sub>4</sub> and K/CoAl<sub>2</sub>O<sub>4</sub> were also prepared by impregnating the corresponding precursors with an aqueous solution of KNO<sub>3</sub>, followed by drying and calcination at 700 °C to give the K/Co molar ratio of 0.04. The precursors for Co<sub>3</sub>O<sub>4</sub> and CoAl<sub>2</sub>O<sub>4</sub> were obtained with the same co-precipitation procedure for hydrotalcite except for different Co/Al molar ratios (Co/Al = ∞ for Co<sub>3</sub>O<sub>4</sub> while Co/Al = 0.5 for CoAl<sub>2</sub>O<sub>4</sub>).

### 2.2. Catalyst characterization

BET surface areas of the catalysts were measured by N<sub>2</sub> adsorption at –196 °C using a Micromeritics ASAP 2010 apparatus. The X-ray diffraction (XRD) patterns were recorded with a PANalytical X'Pert-Pro powder X-ray diffractometer, using Cu K<sub>α</sub> monochromatized radiation (λ = 0.1541 nm) at a scan speed of 5°/min.

Temperature programmed reduction (TPR) experiments were carried out on a Micromeritics AutoChem II 2920 automated catalyst characterization system. 100 mg of a catalyst was loaded into a U-shape quartz reactor and pretreated in Ar at 400 °C for 1 h. Then, after cooling to room temperature, the flowing gas was switched to a 10 vol% H<sub>2</sub>/Ar, and the catalyst was heated to 900 °C at a ramping rate of 10 °C/min.

X-ray photoelectron spectra (XPS) of the catalysts were conducted on an AMICUS apparatus with a Mg K<sub>α</sub> radiation (1253.6 eV, 10 kV, 20 mA, 200 W). The binding energy (BE) values were referenced to the C 1s peak taken as 284.6 eV.

Oxygen adsorption was carried out with a BT2.15 heat-flux calorimeter as described earlier [22]. Prior to the measurement, a catalyst sample was preheated in a special treatment quartz cell in He from room temperature to 500 °C and held at that temperature for 1 h. Then, the sample was outgassed in the cell at 500 °C for 0.5 h under high vacuum. After being cooled to room temperature, the sample was transferred to a side-armed Pyrex vessel and sealed in a

Pyrex capsule. The capsule can minimize the possible contamination in the high vacuum system in the course of thermal equilibrium (6–8 h) with the calorimeter. After thermal equilibrium was reached, the capsule was broken by a vacuum feedthrough and fresh catalyst was exposed. The microcalorimetric data were then collected by sequentially introducing small doses (1–10 μmol) of O<sub>2</sub> onto the sample until it became saturated (5–6 Torr).

Transient response experiment was performed in a fixed-bed flow reactor. Prior to the experiment, a catalyst sample was pretreated in He flow at 500 °C for 1 h and then cooled to 300 °C. 5000 ppm of N<sub>2</sub>O in He was then allowed to pass through the catalyst for a certain time. The outlet gas composition was monitored online by a mass spectrometer (Omini-star, GSD-300), with *m/z* of 44, 28, and 32 representing N<sub>2</sub>O, N<sub>2</sub>, and O<sub>2</sub>, respectively.

### 2.3. Activity tests

Catalytic performance was evaluated in a quartz tube fixed-bed reactor using 100 mg (40–60 mesh) of a catalyst diluted with 400 mg of quartz sand. Before the test, the catalyst was pretreated in He at 500 °C for 1 h, followed by cooling to the reaction temperature in the same atmosphere. Then a reacting gas containing 500 ppm N<sub>2</sub>O in He was introduced in the reactor at a flow rate of 50 mL/min (STP). When O<sub>2</sub> and/or H<sub>2</sub>O were introduced in the feed gas, their concentrations were fixed at 4% and 2.6%, respectively. The outlet gas composition was analyzed online with a gas chromatograph equipped with Porapak Q and Molecular Sieve 13X columns and a thermal conductivity detector. Before analysis, the reaction proceeded at each temperature for 30 min to reach a steady state.

## 3. Results and discussion

### 3.1. Effect of alkali metals on the catalytic activities of the Co-Al catalysts

To precisely investigate the effect of doping alkali metals on the catalytic performance of the Co-Al-500 catalyst, the residual Na<sup>+</sup> resulting from the precipitating agent (Na<sub>2</sub>CO<sub>3</sub> and NaOH) must be removed substantially from the catalyst surface by repetitive washing. The ICP analyses of the Co-Al-500 samples showed that the Na/Co atomic ratio was lower than 5 × 10<sup>–4</sup>, two orders of magnitude lower than our investigated doping amount. It therefore allows us to investigate the additive effect of alkali metals without considering the possible effect of the residual Na<sup>+</sup>. Fig. 1

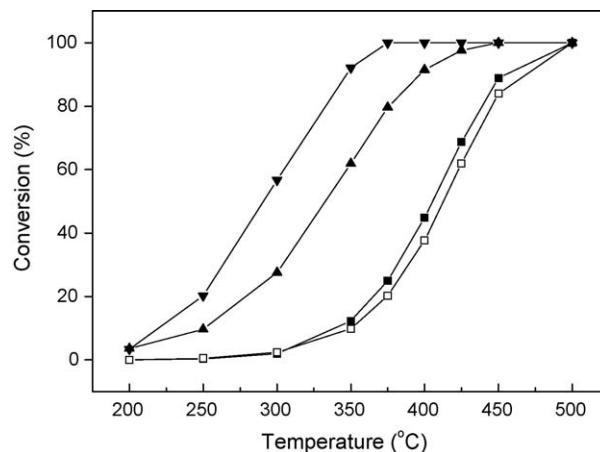
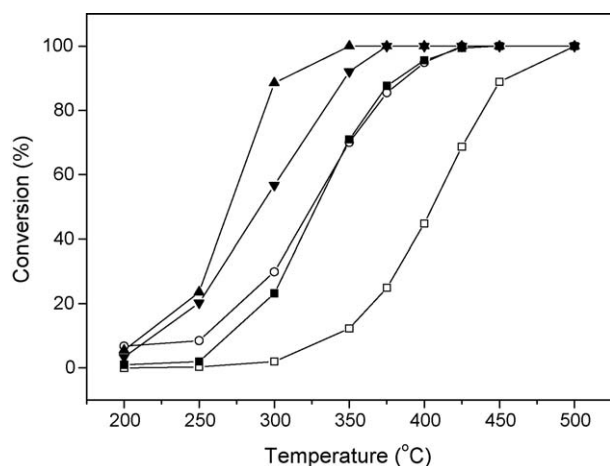


Fig. 1. Conversion of N<sub>2</sub>O as a function of reaction temperature over Co-Al-500 (■), 0.04Na/Co-Al-500 (□), 0.04K/Co-Al-500 (▲), and 0.04K/Co-Al-500 (▼). Reaction conditions: 500 ppm N<sub>2</sub>O, He balance; W/F = 0.12 g s mL<sup>–1</sup>.



**Fig. 2.** Conversion of N<sub>2</sub>O as a function of reaction temperature over different K/Co-Al-500 catalysts with K/Co atomic ratio of 0 (□), 0.02 (○), 0.04 (▼), 0.08 (▲), and 0.12 (■). Reaction conditions: 500 ppm N<sub>2</sub>O, He balance; W/F = 0.12 g s mL<sup>-1</sup>.

illustrates the N<sub>2</sub>O conversions as a function of the reaction temperature over the different alkali metal-doped Co-Al-500 catalysts. It can be seen that doping with either Na<sup>+</sup> or K<sup>+</sup> significantly enhanced the catalytic activity of the Co-Al-500 catalyst while doping with Li<sup>+</sup> resulted in a slight decrease of the activity. In particular, the promotional effect of K<sup>+</sup> was so remarkable that the reaction temperature for complete decomposition of N<sub>2</sub>O was lowered by 125 °C when the atomic ratio of K to Co equaled to 0.04. Such a pronounced enhancement in activity by doping K<sup>+</sup> was also previously observed in alkali metal-doped Co<sub>3</sub>O<sub>4</sub> [17]. Subsequently, we investigated the influence of the doping amount of K<sup>+</sup> on the Co-Al-500 catalyst. It can be seen from Fig. 2 that doping even a very small amount of K<sup>+</sup> (K/Co = 0.02) gave rise to a remarkable increase of the catalytic activity. The activity increased with increasing the K amount until the optimal value of K/Co at 0.08. A further increase in the K content (K/Co = 0.12) induced a decrease in the N<sub>2</sub>O decomposition activity, which may be caused by the partial coverage of the active sites with K<sup>+</sup>. This can also be seen from the change in the specific surface areas upon doping with K<sup>+</sup> (Table 1). When the K/Co ratio increased from 0 to 0.08, the specific surface area had only a slight decrease. However, when the doping amount of K<sup>+</sup> was further increased from K/Co ratio of 0.08 to 0.12, the specific surface area significantly decreased from 101 to 85 m<sup>2</sup>/g. This result indicates that excess

**Table 1**

Specific surface areas and turnover frequencies (TOFs) of different Co-Al catalysts.

Catalysts	BET surface area (m <sup>2</sup> /g)	TOF <sup>a</sup> (s <sup>-1</sup> ) × 10 <sup>6</sup>
Co-Al-500	110	0.05
Co-Al-700	52	0.04
0.02K/Co-Al-500	103	1.55
0.04K/Co-Al-500	106	4.11
0.08K/Co-Al-500	101	4.43
0.12K/Co-Al-500	85	0.38
0.04K/Co-Al-700	78	10.21
0.04K/Co-Al-800	64	9.47
0.04K/Co-Al-900	40	5.09
0.04K/Co-Al-1000	22	1.16
Co <sub>3</sub> O <sub>4</sub> -700	17	0.04
0.04K/Co <sub>3</sub> O <sub>4</sub> -700	38	3.04
0.04K/CoAl <sub>2</sub> O <sub>4</sub> -700	138	0.008

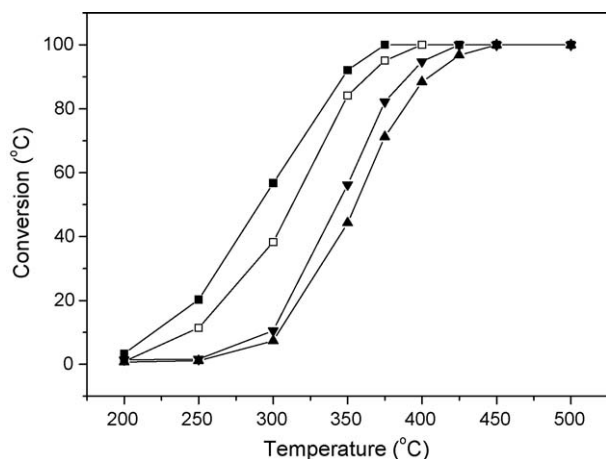
<sup>a</sup> The TOFs were evaluated at 250 °C under conditions of 500 ppm N<sub>2</sub>O + He and a W/F = 0.12 g s mL<sup>-1</sup>.

amount of K indeed brought about partial coverage of the Co-Al oxide surface. Compared to the K/Co<sub>3</sub>O<sub>4</sub> catalyst [17,23], our present K/Co-Al-500 catalyst seems to require a higher K/Co ratio to obtain the best catalytic performance. This might be because a part of K<sup>+</sup> are deposited on the alumina instead of the cobalt oxide surface, thus without interaction with the Co<sup>2+</sup> active sites.

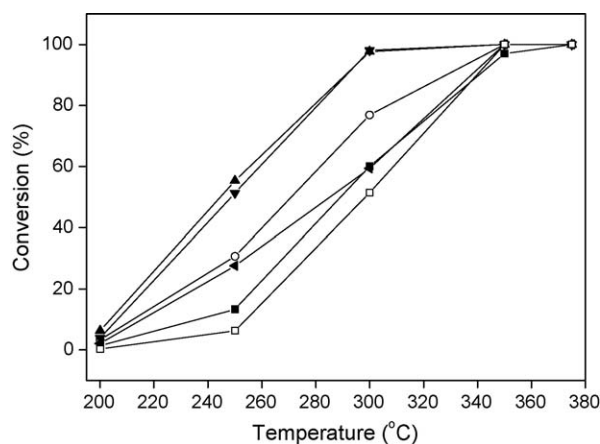
The effects of oxygen and/or water steam on N<sub>2</sub>O decomposition over the 0.04K/Co-Al-500 are shown in Fig. 3. The presence of 4% O<sub>2</sub> caused only a slight decrease of the catalytic activity, whereas the presence of 2.6% H<sub>2</sub>O or the simultaneous presence of 4% O<sub>2</sub> and 2.6% H<sub>2</sub>O brought about a remarkable decrease in the catalytic activity, with the temperature for complete decomposition of N<sub>2</sub>O being raised by about 100 °C. Such a poisoning effect of H<sub>2</sub>O on the 0.04K/Co-Al-500 was similar to that of the Co<sub>3</sub>O<sub>4</sub> catalyst [17], in which water was proposed to be adsorbed on the active sites leading to inhibition of N<sub>2</sub>O decomposition.

### 3.2. Effect of calcination temperature

In most investigations on the alkali metal promoted catalysts for N<sub>2</sub>O decomposition, the catalysts were usually calcined at or below 500 °C prior to the activity tests [15–18]. In the present work, to further improve the interaction between K and the active sites (e.g., Co<sup>2+</sup>), we elevated the calcination temperature to investigate its effect on the catalytic activity of the 0.04K/Co-Al. As shown in Fig. 4, when the calcination temperature was raised from 500 °C to 700–800 °C, the activity of the 0.04K/Co-Al increased significantly. With further elevating the calcination temperature to



**Fig. 3.** Conversion of N<sub>2</sub>O as a function of reaction temperature over the 0.04K/Co-Al-500 under different feeding conditions. (■) 500 ppm N<sub>2</sub>O in He; (□) 500 ppm N<sub>2</sub>O + 4% O<sub>2</sub>; (▼) 500 ppm N<sub>2</sub>O + 2.6% H<sub>2</sub>O; and (▲) 500 ppm N<sub>2</sub>O + 4% O<sub>2</sub> + 2.6% H<sub>2</sub>O. W/F = 0.12 g s mL<sup>-1</sup>.



**Fig. 4.** Conversion of N<sub>2</sub>O as a function of reaction temperature over 0.04K/Co-Al catalysts which were calcined at different temperatures. (■) 500 °C; (○) 600 °C; (▲) 700 °C; (▼) 800 °C; (◄) 900 °C; and (□) 1000 °C. Reaction conditions: 500 ppm N<sub>2</sub>O, He balance; W/F = 0.12 g s mL<sup>-1</sup>.

900 °C, the resultant catalyst had some loss in its activity. Even though, it was still more active than the 0.04K/Co-Al-500. To our knowledge, this is the first report that high-temperature calcination treatment can largely increase the activity of the K-promoted Co-based catalyst for N<sub>2</sub>O decomposition although the promoting role of K<sup>+</sup> on the Co<sub>3</sub>O<sub>4</sub> has been reported earlier [17]. It is noted that the specific surface areas of the 0.04K/Co-Al samples decreased continuously with the elevation of the calcination temperature, which is in contrary to the trend of the catalytic activity. Clearly, there are factors other than the specific surface area governing the catalytic activity of the K/Co-Al catalysts. According to literature [24], the interaction between a dopant and the substrate became strong with increasing the calcination temperature. Such a strong interaction, we believe, should be responsible for the enhanced activity of the high-temperature calcined K/Co-Al catalysts. On the other hand, when the sample was calcined at a temperature as high as above 900 °C, the decline in surface area became so significant that it caused some loss in activity.

We also found that the Co-Al catalyst resulting from the hydrotalcite precursor was more active than the Co<sub>3</sub>O<sub>4</sub> upon doping with K and being subject to a high-temperature treatment. As shown in Fig. 5, both the Co-Al-700 and Co<sub>3</sub>O<sub>4</sub>-700 catalysts without doping with K had a great loss in activity upon calcination at 700 °C; the complete decomposition of N<sub>2</sub>O was attained only at above 550 °C. However, doping with K followed by calcination at 700 °C greatly increased the catalytic activity, both for the Co-Al and for the Co<sub>3</sub>O<sub>4</sub> catalysts. Such a promoting effect was more pronounced for the Co-Al catalyst, the full conversion of N<sub>2</sub>O was already reached at 300 °C over the 0.04K/Co-Al-700 whereas only 80% of N<sub>2</sub>O conversion was obtained at the same temperature over the 0.04K/Co<sub>3</sub>O<sub>4</sub>-700. To quantitatively compare the catalytic activities of the Co-Al mixed oxides and the Co<sub>3</sub>O<sub>4</sub>, we calculated the turnover frequency (TOF) by assuming Co as the active sites for N<sub>2</sub>O decomposition. From Table 1 one can see that the TOF of the Co-Al-700 was  $0.04 \times 10^{-6} \text{ s}^{-1}$ , which was the same as that of the Co<sub>3</sub>O<sub>4</sub>-700. However, upon doping with K (K/Co = 0.04), the TOF of the Co-Al increased by a factor of 255, while the TOF of the Co<sub>3</sub>O<sub>4</sub> increased only by a factor of 76. Apparently, compared with the previously reported K/Co<sub>3</sub>O<sub>4</sub> [17], the Co-Al catalyst had a better interaction with K for maximizing the promoting role of K. Moreover, by comparing the specific surface areas shown in Table 1, one can see that the non-doped Co-Al catalyst had a significant loss in surface area after high-temperature treatment (110 m<sup>2</sup>/g for Co-Al-500 and 52 m<sup>2</sup>/g for Co-Al-700). In contrast,

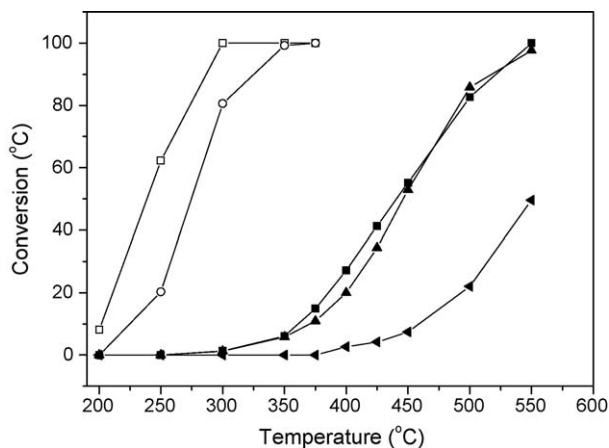
such a decrease in surface areas was alleviated remarkably by doping of K<sup>+</sup> (106 m<sup>2</sup>/g for 0.04K/Co-Al-500 and 78 m<sup>2</sup>/g for 0.04K/Co-Al-700). This result indicates that doping with K suppresses sintering of the particles to a certain extent. A similar phenomenon was also observed by other researchers in the K/Co<sub>3</sub>O<sub>4</sub> catalyst [17].

High-temperature calcination not only greatly enhanced the catalytic activity of the K/Co-Al, but also largely improved the stability of the catalyst. As shown in Fig. 6, in the simultaneous presence of 4% O<sub>2</sub> and 2.6% H<sub>2</sub>O, the Co-Al-500 had an initial N<sub>2</sub>O conversion of 66% at 500 °C, which continuously went down to 45% after 45 h of time on stream. In contrast, the 0.04K/Co-Al-500 gave an initial N<sub>2</sub>O conversion of 80% at a reaction temperature of 375 °C, which was only slightly decreased to 75% after 45 h run. In particular, the 0.04K/Co-Al-700 catalyst presented a fairly stable reactivity, with the N<sub>2</sub>O conversion remaining at a high level (92%) at 360 °C over 45 h run. The remarkably high activity and stability of the 0.04K/Co-Al-700 in a stream containing both O<sub>2</sub> and H<sub>2</sub>O would make it a promising candidate for N<sub>2</sub>O removal in a realistic atmosphere.

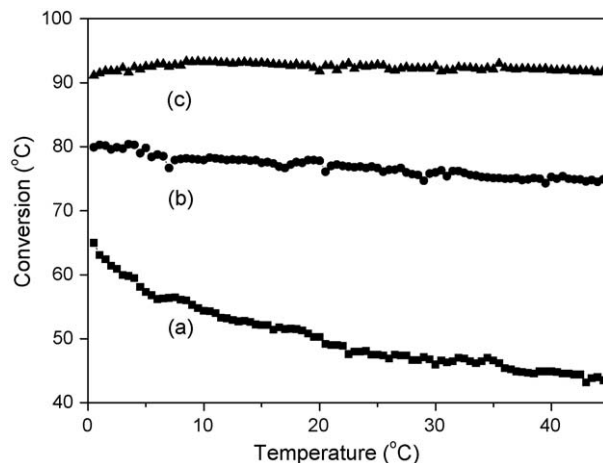
In view of the strongly exothermic nature of the N<sub>2</sub>O decomposition, the thermal stability of a catalyst is even of the same importance as the activity. In our previous work, we developed a highly thermal stable catalyst by incorporating active Ir component into the framework of hexaaluminate [25]. Although the mixed oxides resulting from hydrotalcite have a lower thermal stability than the hexaaluminate, our above work has demonstrated that doping with K can improve the thermal stability of the mixed oxides to some extent. More intriguing, it can largely enhance the catalytic activity by modifying the electronic properties of the mixed oxides. Thus, for the decomposition of low concentration of N<sub>2</sub>O where the bed temperature rise is not so remarkable, our present 0.04K/Co-Al-700 catalyst, which has high activity and good tolerance to inhibitory gases (O<sub>2</sub> and steam), will represent one of feasible choices for N<sub>2</sub>O abatement.

### 3.3. Revealing the underlying reason for activity enhancement of the K-doped catalysts

The above results have shown that the addition of K largely enhanced the reactivity and stability of the Co-Al mixed oxides for N<sub>2</sub>O decomposition. In this section, we will uncover the underlying reason for such an enhancement by using a combination of characterization techniques.

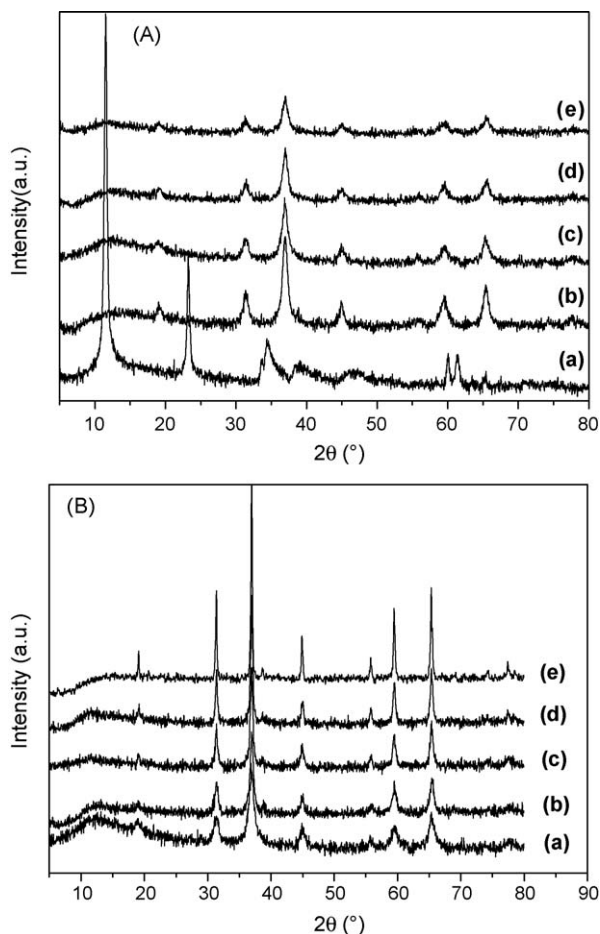


**Fig. 5.** Conversion of N<sub>2</sub>O as a function of reaction temperature over Co-Al-700 (■), Co<sub>3</sub>O<sub>4</sub>-700 (▲), 0.04K/Co-Al-700 (□), 0.04K/Co<sub>3</sub>O<sub>4</sub>-700 (○), and 0.04K/CoAl<sub>2</sub>O<sub>4</sub>-700 (▲). Reaction conditions: 500 ppm N<sub>2</sub>O, He balance; W/F = 0.12 g s mL<sup>-1</sup>.



**Fig. 6.** Conversion of N<sub>2</sub>O with time on stream over (a) Co-Al-500 at 500 °C, (b) 0.04K/Co-Al-500 at 375 °C, and (c) 0.04K/Co-Al-700 at 360 °C. Reaction conditions: 500 ppm N<sub>2</sub>O, 4% O<sub>2</sub>, 2.6% H<sub>2</sub>O, He balance; W/F = 0.12 g s mL<sup>-1</sup> for (a) and (b), W/F = 0.11 g s mL<sup>-1</sup> for (c).

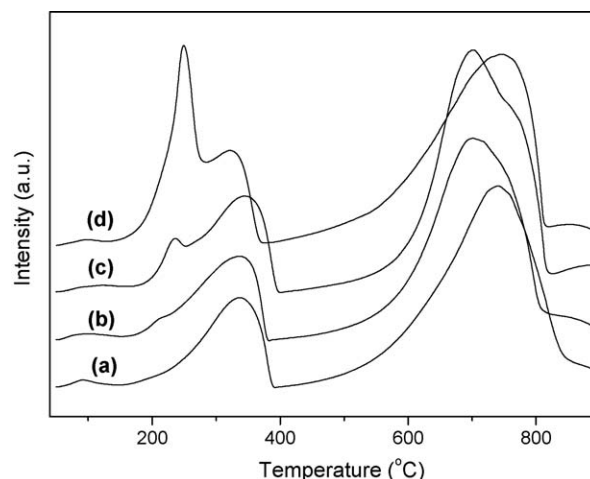




**Fig. 7.** XRD patterns of (A) Co-Al-HT: (a) and K/Co-Al-500 catalysts with K/Co atomic ratio of (b) 0; (c) 0.04; (d) 0.08; and (e) 0.12. (B) 0.04K/Co-Al catalysts calcined at different temperatures. (a) 500 °C; (b) 700 °C; (c) 800 °C; (d) 900 °C; and (e) 1000 °C.

### 3.3.1. XRD characterization

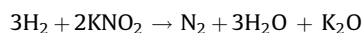
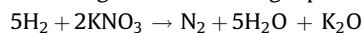
The XRD patterns of the catalysts with different K loadings are shown in Fig. 7. For comparison, the XRD pattern of the non-calcined hydrotalcite precursor (denoted as Co-Al-HT) is also presented. It can be seen that the Co-Al-HT sample has a typical XRD pattern of hydrotalcite, no other impurity phase (such as  $\text{CoCO}_3$ ) was found. For the calcined K-promoted Co-Al oxide samples, all the patterns were typical of spinel structure, and the presence of K appeared to make the peaks broader. No any K species could be detected by XRD, indicating that the  $\text{K}^+$  cations are highly dispersed on the surface of the mixed oxides. Moreover, the intensities of the XRD peaks increased with a rise of the calcination temperature. In particular, when the calcination temperature went up to 1000 °C, the peaks became very sharp, which suggests that more Co cations migrate into tetrahedral sites of  $\gamma\text{-Al}_2\text{O}_3$  to form a non-reducible  $\text{CoAl}_2\text{O}_4$  phase at such a high temperature [26]. The lack of reducible Co sites in the  $\text{CoAl}_2\text{O}_4$  phase makes it inactive for catalyzing  $\text{N}_2\text{O}$  decomposition. Therefore, the activity loss of the 0.04K/Co-Al-1000 catalyst should be caused by a part of catalytically active Co-Al mixed oxides transforming into the inactive  $\text{CoAl}_2\text{O}_4$  spinel phase. To confirm this, we prepared K/ $\text{CoAl}_2\text{O}_4$ -700 sample by decreasing the Co/Al molar ratio in the synthesis mixture to a stoichiometric ratio of 1/2. The  $\text{H}_2$ -TPR measurement showed that most of the Co species in this sample cannot be reduced below 600 °C, suggesting that  $\text{CoAl}_2\text{O}_4$  is the dominant phase in this sample. As expected, this sample gave a rather poor activity for  $\text{N}_2\text{O}$  decomposition (Fig. 5).



**Fig. 8.** TPR profiles of (a) Co-Al-500; (b) 0.04K/Co-Al-500; (c) 0.08K/Co-Al-500; and (d) 0.12K/Co-Al-500.

### 3.3.2. $\text{H}_2$ -TPR results

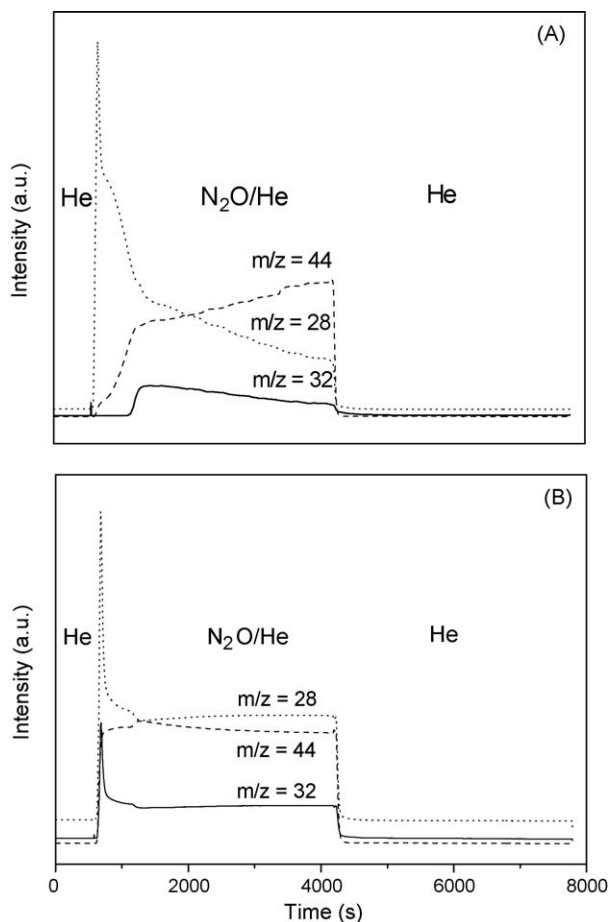
It is generally accepted that oxygen desorption is a critical step for  $\text{N}_2\text{O}$  decomposition process [4]. Oxygen mobility on the catalyst surface is therefore an important factor affecting the reactivity of the catalyst.  $\text{H}_2$ -TPR is a simple and effective tool to evaluate the mobility of oxygen. Fig. 8 compares the  $\text{H}_2$ -TPR profiles of the catalysts with different K/Co ratios. It can be seen that the Co-Al-500 catalyst presented two broad reduction peaks around 200–400 °C and 600–800 °C, which can be attributed to the reduction of Co ion in  $\text{Co}_3\text{O}_4$  and in  $\text{CoAl}_2\text{O}_4$ , respectively [27]. The addition of K brought about a new reduction peak at low temperature region (210–230 °C), whose intensities increased with raising the K content. Apparently, this new peak should be associated with the presence of K. To make a correct assignment of this peak, we detected the effluent gas by mass spectroscopy (MS) and found that a sharp peak with  $m/z$  of 28 (corresponding to  $\text{N}_2$ ) coincides with this new peak. In order to confirm that  $m/z$  28 comes from  $\text{N}_2$  instead of CO, we compared the profile of  $m/z$  = 28 with that of  $m/z$  = 14, and found that the two curves coincide very well (not shown). Accordingly, we believe that  $\text{N}_2$  was indeed produced in the TPR process of the K-promoted catalysts. Considering that  $\text{KNO}_3$  has a high decomposition temperature [28] and  $\text{H}_2$  can promote its decomposition by reducing the  $\text{NO}_3^-$  or  $\text{NO}_2^-$  ions, we assigned this new peak to the reduction of  $\text{NO}_3^-$  or  $\text{NO}_2^-$  by  $\text{H}_2$ , according to the following equation:



When the doping amount of K increased from K/Co of 0.02 to 0.08, the peaks corresponding to the reduction of Co species did not change remarkably. However, when the K content increased further to a K/Co ratio of 0.12, the peak due to the reduction of  $\text{KNO}_3$  increased significantly, while the peak corresponding to the reduction of  $\text{Co}_3\text{O}_4$  had a large decrease. Since  $\text{Co}^{2+}$  was reported to be the active site for  $\text{N}_2\text{O}$  decomposition on  $\text{Co}_3\text{O}_4$  catalyst [17], doping of excess amount of K clearly blocked the active sites, which resulted in a decrease of the catalytic activity.

### 3.3.3. Transient kinetic experiments

Transient responses of  $\text{N}_2\text{O}$ ,  $\text{N}_2$ , and  $\text{O}_2$  induced by a step variation in the concentration of  $\text{N}_2\text{O}$  over the Co-Al-500 and the 0.04K/Co-Al-500 were conducted at 300 °C, with  $W/F$  of 0.2 and 0.02  $\text{g s mL}^{-1}$ , respectively. The choice of temperature and  $W/F$  is to maintain the  $\text{N}_2\text{O}$  conversions on the two catalysts at almost the same low values (<10%). As can be seen in Fig. 9A, upon the flow

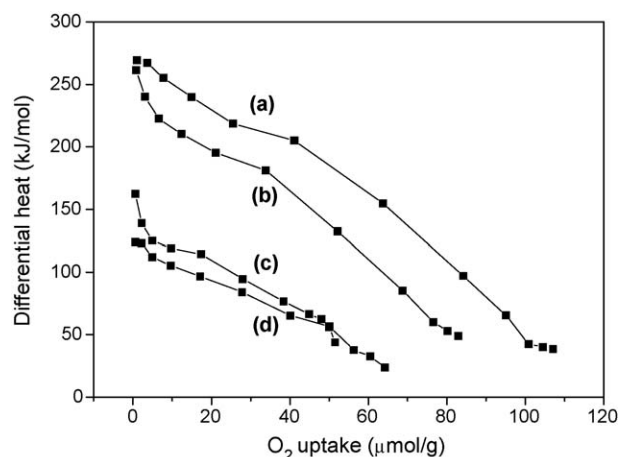


**Fig. 9.** Transient response curves of  $\text{N}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{O}_2$  induced by a step variation in the feeding composition over (A) Co-Al-500, at 300 °C,  $W/F = 0.2 \text{ g s mL}^{-1}$ ; (B) 0.04K/Co-Al-500, at 300 °C,  $W/F = 0.02 \text{ g s mL}^{-1}$ .

gas over the Co-Al-500 catalyst being switched from He to  $\text{N}_2\text{O}/\text{He}$ , the evolution of  $\text{N}_2$  ( $m/z = 28$ ) occurred instantly, and was even more rapidly than that of  $\text{N}_2\text{O}$  ( $m/z = 44$ ). This result indicates that  $\text{N}_2\text{O}$  decomposition to  $\text{N}_2$  is a fast step. On the contrary, there was a significant delay in the appearance of  $\text{O}_2$  ( $m/z = 32$ ) over the Co-Al-500 catalyst, implying that  $\text{O}_2$  desorption from this catalyst surface is a rate-limiting step. However, it is noted that there was no any delay in  $\text{O}_2$  desorption over the 0.04K/Co-Al-500 catalyst. This result suggests that the addition of K greatly facilitates the desorption of oxygen from the catalyst surface and thereby enhances the catalytic activity.

### 3.3.4. $\text{O}_2$ adsorption

To further demonstrate the effect of K addition on the oxygen mobility, we used microcalorimetry to quantitatively measure the adsorption heat and adsorption amount of  $\text{O}_2$  on the K/Co-Al catalysts. Fig. 10 shows the differential heat of oxygen adsorption as a function of oxygen coverage on the K/Co-Al-500 catalysts with different K loadings. The initial adsorption heat of  $\text{O}_2$  on the Co-Al-500 catalyst was 270 kJ/mol, indicating that  $\text{O}_2$  is strongly adsorbed on this catalyst surface. However, the addition of K led to a marked decrease in both adsorption heat and uptake of  $\text{O}_2$ . For example, when K/Co ratio was 0.08, the initial adsorption heat of  $\text{O}_2$  dropped to 162 kJ/mol and the  $\text{O}_2$  uptake was only 40  $\mu\text{mol/g}$ . This result suggests that the addition of K significantly weakens the Co–O bond and thereby facilitates the oxygen mobility. Fig. 11 presents the differential heat curves on the 0.04K/Co-Al catalysts which had been calcined at different temperatures. It is clear that with an

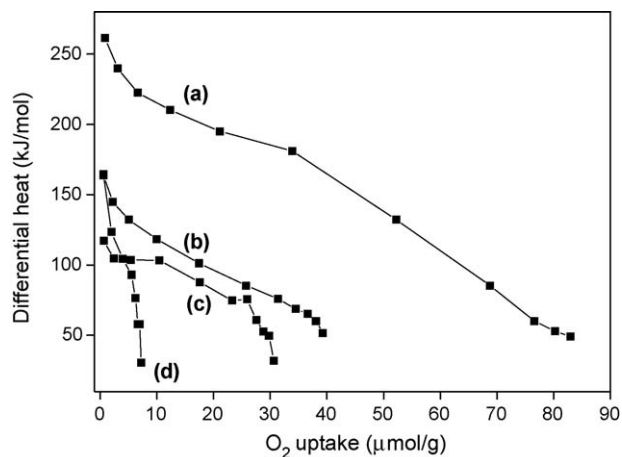


**Fig. 10.** Differential heats of  $\text{O}_2$  adsorption as a function of  $\text{O}_2$  uptake on the K/Co-Al-500 catalysts with K/Co atomic ratio of (a) 0; (b) 0.04; (c) 0.08; and (d) 0.12.

increase of the calcination temperature, both the adsorption heat and the uptake of oxygen had a remarkable decrease, suggesting that high-temperature treatment of the 0.04K/Co-Al catalysts further weakens the binding of oxygen to the catalyst surface. Since oxygen desorption from the catalyst surface is suggested as a rate-determining step in the decomposition of  $\text{N}_2\text{O}$  [4], the weakened binding of oxygen to the catalyst surface by doping with K and by calcining the doped catalyst at a high-temperature will facilitate the desorption of oxygen from the catalyst surface, resulting in an enhanced catalytic activity. This conclusion agrees with our activity test results.

### 3.3.5. XPS results

XPS analysis was carried out to shed more light on the electronic modification by doping K on the Co-Al catalysts. Fig. 12 shows the spectra of the Co-Al-500 and the 0.04K/Co-Al-500 in Co 2p region. For the Co-Al-500 catalyst, the Co  $2p_{3/2}$  binding energy was 780.9 eV, which was higher than that in  $\text{Co}_3\text{O}_4$  catalyst [17]. Doping with K caused Co 2p binding energy shifting to a lower value. The similar trend has been observed in the K/ $\text{Co}_3\text{O}_4$  catalyst [17] and can be interpreted as electron donation from oxygen anions surrounding the alkali cation toward cobalt. Thus, the increase in the electron density of  $\text{Co}^{2+}$  due to doping with K would weaken the Co–O bond and facilitate the oxygen desorption from the catalyst surface.



**Fig. 11.** Differential heats of  $\text{O}_2$  adsorption as a function of  $\text{O}_2$  uptake on the 0.04K/Co-Al catalysts calcined at different temperatures. (a) 500 °C; (b) 600 °C; (c) 700 °C; and (d) 1000 °C.

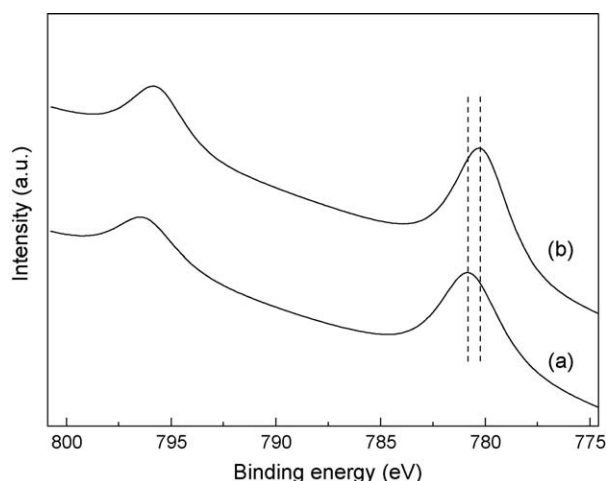


Fig. 12. Co 2p XPS spectra of the K/Co-Al-500 catalysts with K/Co atomic ratio of (a) 0 and (b) 0.04.

According to literature [29], the decomposition of  $\text{N}_2\text{O}$  can be described with the following equations:



In the first step,  $\text{N}_2\text{O}$  adsorbs at the active site, which can be regarded as a charge donation from the catalyst surface to the antibonding orbitals of  $\text{N}_2\text{O}$ , destabilizing the N–O bond and resulting in the formation of  $\text{N}_2$  and a surface O. Subsequently, this surface oxygen can desorb either by combination with another oxygen atom Eq. (2) or by direct reaction with another  $\text{N}_2\text{O}$  Eq. (3). Based on the above reaction pathway, there are two main factors affecting the catalytic activity: the capability for activating  $\text{N}_2\text{O}$  and the desorption of oxygen from the catalyst surface. Our XPS results have shown that addition of K increased electron density on the Co sites, making them more readily donating electrons to the adsorbed  $\text{N}_2\text{O}$ , thus facilitating the activation of  $\text{N}_2\text{O}$ . Moreover, the binding of oxygen to the catalyst surface is significantly weakened by the doping with K and by elevating the calcination temperature, as revealed by our calorimetric results of oxygen adsorption. Therefore, the catalytic activities of the Co-Al mixed oxides are remarkably enhanced due to the promotion of K. One important thing to be emphasized in our work is that the 0.04K/Co-Al-700 exhibited a high catalytic activity and a superior stability even under the simultaneous presence of  $\text{O}_2$  and  $\text{H}_2\text{O}$ . Such an excellent performance highlights its great potential as an industrially important catalyst for  $\text{N}_2\text{O}$  abatement.

## 4. Conclusions

In summary, it was found that doping with K on the Co-Al mixed oxides resulting from the hydrotalcite significantly enhanced the catalytic activity and reaction stability. Calcination treatment at 700–800 °C could further increase the activity, which endows the K/Co-Al catalyst with a combination of advantages: high activity at low temperatures, high thermal stability and good tolerance to  $\text{O}_2$  and water vapor. The role of K is to facilitate oxygen desorption from the catalyst surface by weakening the Co–O bond, and high-temperature treatment makes such a promotional effect more pronounced.

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